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# ACIDIFICATION OF SHALLOW GROUNDWATERS DURING THE SPRING MELT PERIOD

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## MANAGEMENT PERSPECTIVE

The discharge of ground water to surface water bodies has been shown to be a major factor in minimizing the effects of acid loading on these surface waters. The acidity of ground water is significantly less than that of surface waters in the same basin because the aquifer materials neutralize a large part of the acidity of the infiltrating precipitation. However, the data presented in this paper indicate that there is a close relationship between depressions in ground water pH and the strong acid loadings which accompany rain and snow melt events. That is, each rapid, large increase in acid loading results in a rapid decrease in pH. These temporary depressions in ground water pH following snow melt and rain are significant events in the process of basin acidification. If ground water is becoming acidified and if the acid loadings remain the same, the ability of the entire watershed to withstand the effects of acidic precipitation is compromised. This may represent the early stages of a development towards the levels of ground water acidification observed in the Scandinavian Peninsula.

## PERSPECTIVE DE GESTION

L'écoulement d'eau souterraine dans les plans d'eau de surface constitue un facteur très important dans la réduction des effets de la charge acide dans ces eaux. L'acidité est beaucoup plus basse dans l'eau souterraine que dans l'eau de surface, dans le même bassin hydrographique, parce que les substances de la nappe aquifère neutralisent une grande partie de l'acidité causée par les précipitations. Les données présentées dans ce rapport permettent toutefois d'établir un rapport étroit entre l'abaissement du pH de l'eau souterraine et les fortes charges acides qui se retrouvent à l'occasion des pluies et de la fonte des neiges. Ainsi donc, toute agumentation soudaine, importante, de la charge acide se traduit par un abaissement soidan du pH. Ces baisses temporaires du pH de l'eau souterraine par suite de pluies ou de la fonte des neiges constitutent des épisodes importants dans le processus d'acidification du bassin. Si l'eau souterraine s'acidifie et si les charges acides demeurent les mêmes, la faculté du bassin hydrographique dans son ensemble de résister aux effets des précipitations acides se trouve compromise. Il peut donc s'agir des premières étapes du processus qui mène à des niveaux d'acidification des eaux souterraines comme ceux que l'on a observés en Scandinavie.

ABSTRACT

During the spring of 1985 shallow recharge area groundwaters at depths less than one metre in the Turkey Lakes watershed were observed to undergo short term (1 to 10 days) pH and alkalinity depressions associated with both rain and snow melt events. At the same time the concentrations of $K^+$ in the groundwater increased. Observations suggest that, if, during an individual loading event, the loading rate of Hydrogen ions ($H^+$) exceeds the rate at which alkalinity is made available through carbonate weathering reactions, increased alumino-silicate alteration can occur. Thus alumino-silicate alteration may occur in groundwater systems with measurable carbonate alkalinity.

## RÉSUMÉ

Au cours du printemps de 1985, les eaux souterraines se trouvant à moins d'un mètre de profondeur dans une zone d'alimentation du bassin hydrographique des lacs Turkey ont subi une baisse de leur pH et une perte d'alcalinité sur une courte période (de un à dix jours), et ce, à la suite de la fonte de neige et de précipitations en pluie. On y a également constaté une augmentation du nombre d'ions $K^+$ au cours de la même période. D'après ces observations, on peut supposer que si, au cours d'une seule manifestation, le taux de charge en ions d'hydrogène ($H^+$) dépasse le taux d'alcalinisation due à la désagrégation de carbonate, il se produit une plus grande altération des alumino-silicates, notamment dans les nappes d'eau souterraine dont l'alcalinité carbonatée est mesurable.

## INTRODUCTON

Studies in the Turkey Lakes watershed (TLW), located north of Sault Ste Marie, Ontario, Canada (Figure 1) are examining the role of groundwater in modifying the effects of acidic precipitation on surface water chemistry. Results of these and other studies show that the characteristic composition and structure of the surficial deposits in a given watershed and the pathways that subsurface water follows through such materials are important factors in watershed acidification (Bache 1984; Booty and Kramer 1984; Craig and Johnston 1987). This study is part of an investigation of the relationship between these characteristics of the surficial deposits and the groundwater chemistry.

Previous studies at both the Turkey Lakes and Harp Lake, Ontario watersheds have investigated the capacity of groundwater discharge to minimize pH depression in surface waters during acid loading events. During runoff events, naturally occurring oxygen-18 was used as a tracer in order to produce stream hydrographs which show the separate pre-storm and storm components of the runoff (Bottomley et al. 1984, 1986). Results from those studies indicate that 40% to 90% of the peak storm and snowmelt runoff in the TLW was composed of pre-event groundwater. Because the alkalinity of the groundwater is much greater than that of the precipitation in the region, groundwater discharge results in significant neutralization of runoff acidity. It follows that any reduction in the alkalinity of the groundwater would result in increased sensitivity to acid loadings in the surface waters into which the

groundwaters are discharged. With these possible effects on surface water chemistry in view, this paper examines pH and alkalinity depressions observed in shallow groundwaters during the spring melt period in the Turkey Lakes watershed.

## SITE DESCRIPTION

The Turkey Lakes watershed is subjected to 30-35 kg/ha/yr $SO_4^{2-}$ atmospheric loadings. Significantly there is considerable acid neutralization capacity in the surficial deposits. Much of the watershed is covered by a thin, discontinous till less than two metres thick; accumulations up to 70 m however, are found in some valleys (Elliot 1985). The till can be divided into two general types (Cowell and Wickware 1983): the upper ablation till which is less than one metre thick, is highly permeable ($1x10^{-3}$ cm/sec ) and contains minute amounts of carbonate. The basal till is much less permeable ($1x10^{-5}$ cm/sec) and contains larger amounts of carbonate (0.05%) (Johnston and Craig 1986). The watershed is underlain by Precambrian greenstones, with some granite to the northeast. The bedrock acts as a confining layer and has little direct affect on groundwater chemistry.

Large spatial variations in groundwater chemistry exist, with pH ranging from 5.2 to 8.1 and alkalinities from 0.02 to 1.2 meq/L across the watershed. At all test locations in the basin, pH and alkalinity increase with sample depth. The groundwater chemistry is described in detail elsewhere (Craig and Johnston 1987)

## HEADWATER LAKE STUDY AREA

Surface waters in the Batchawana Lake sub-basin show degradation due to acid loadings. This is demonstrated by pH depression and elevated aluminium levels during wet loading events (Nicolson 1983). Because of its thin tills, and their low carbonate content, this area is the most poorly buffered sub-basin in the watershed.

Test wells here are located on a hillside at site HU (Figure 1). Well HU-0.67 is located about 8.8 metres above lake level in a groundwater recharge area. The thickness of till at this site corresponds to the depth of the well (0.67 m).

Acid neutralization capacities (ANC) of the tills were measured using samples taken from a core obtained at the north-east corner of Lower Batchawana Lake, near the HU site. ANC's measured in the shallow overlying ablation till (zero to one metre thickness) are markedly less than those observed in the basal till. At the contact between the two tills the change in the ANC is abrupt.

### Method

During the spring melt period of 1985 (March and April) groundwater samples were collected in response to hydrologic events and weather conditions. The pH and specific conductance were measured in a field laboratory within an hour of sampling, and the alkalinity was measured on a filtered (0.45µ) sample within one day of collection (Metrohn 682 titroprocessor). Samples were filtered (0.45µ) and stored for the analysis of major anions (Dionex 2010i ion chromatograph) and cations in accordance with methods outlined by the Department of the Environment (Anon. 1979).

## RESULTS

It rained twice during the study period. Within a 15 hour period from 11:00 PM March 26 to 2:00 PM on March 27, before the onset of snow melt, the site received 19.2 mm of rain (pH 3.9). On March 29, 3.6 mm of rain fell between 3:00 AM and 9:00 AM. Finally, on April 14 a rise in temperature caused the onset of snow melt (average pH approx. 4.5).

At well HU-0.67, the changes in groundwater level and pH immediately prior to and during spring melt are inversely related (Figure 2). The rapid rises in the water table at this site were due to the three separate infiltration events. The March 27 rain infiltrated the snow pack and soil to raise the water table from -0.52 metres to -0.26 metres. The water table level peaked at about 3:00 PM on March 27 and decreased until the rain of March 29 caused a second infiltration event and a subsequent rise in the water table. The groundwater levels then subsided to levels observed prior to the initial rain. After April 1, and until the beginning of snow melt, the groundwater levels were about -0.5 metres, reflecting the lack of snow melt or rain water infiltration during this interval. Then, on April 14, the onset of the major snowmelt period resulted in increased infiltration and a rapid rise in the water table. The daily peaks observed until about April 27 are the result of diurnal variation in the rate of snow melt.

In conjunction with the rises in water table level described above, the groundwater pH decreased from approximately 5.1 to 4.6. Following the rains, the pH recovered over the next 5 or 6 days until it had reached its pre-rain value of 5.1. The groundwater sampling frequency was insufficient to detect any influence of the March 29 rain on the pH values. During the spring snow melt , the rise in the water table was again accompanied by a decrease in pH and once again it reached a minimum of 4.6. The pH did not return to its initial values until after the fall in the water table following the end of spring melt.

Alkalinity followed a pattern similar to the pH (Figure 2), decreasing with rapid rises in the groundwater level. From initial values between 0.02 and 0.03 meq/l prior to the March 27 rain, it decreased to 0.00 meq/l towards the end of the rain. After the sharp decline in the water table following the rains, the alkalinity recovered to a maximum of 0.02 meq/l. With the start of snowmelt and the rise in the water table the alkalinity decreased again to 0.00 meq/l on April 17 and did not recover until after the end of the spring melt.

The samples also showed that as the concentration of $H^+$ increased and the concentration of alkalinity decreased, the concentration of $K^+$ in the groundwater increased sharply (Figure 3). The concentration of other cations ($Ca^{2+}$, $Mg^{2+}$, $Na^+$), however, did not change.

## DISCUSSION AND CONCLUSIONS

As part of the TLW study, Semkin and Jeffries (1985, pers com 1986) have examined the storage and release of contaminants from the snowpack in the Turkey Lakes watershed. Their data, showing loadings of $SO_4^{2-}$ + $NO_3^-$ leaving the bottom of the snow pack, are presented in figure 4. Groundwater pH values for the same period are also shown in figure 4. This figure clearly demonstrates the close relationship between depressions in groundwater pH and the strong acid loadings which accompany rain and snow melt events. That is, each rapid, large increase in acid loading results in rapid decreases in pH.

Temporary depressions in groundwater pH following snow melt and rain are significant events in the process of basin acidification. In the Turkey Lakes watershed, the discharge of groundwater has been shown to be a major factor in minimizing the effects of acid loading on surface waters (Bottomley et al. 1984, 1986). These pH depressions, then, signify the reduced ability of the groundwater and, therefore, of the entire watershed to accept and to neutralize $H^+$ ions.

The ability of surface waters in the TLW to neutralize $H^+$ ions derives chiefly from groundwater alkalinity. Compared with other watersheds in the Canadian Shield, the alkalinity concentrations in the groundwater here are relatively high. This groundwater alkalinity is a result of geochemical weathering of small amounts of carbonate minerals (calcite, dolomite) found in the watershed's tills . The assertion that such weathering is the source of the alkalinity is supported by the

observation that along the sub-surface flowpaths the groundwater can be characterized as evolving from $Ca^{2+}SO_4^{2-}$ dominated water in recharge areas to $Ca^{2+}HCO_3^-$ dominated water in the discharge areas. This evolution corresponds to increasing sediment contact time as the groundwater moves through the flow system (Craig and Johnston 1987).

The ability of any basin to neutralize acid loadings, however, is a function not only of the quantity and type of minerals present in that basin, but also of their availability in the hydrologic cycle to act as acid sinks. Alumino-silicate minerals predominate in the TLW, for example, but hydrolysis reactions with them, although thermodynamically possible, are extremely slow compared with the residence times common for groundwater in this basin. On the other hand, when calcite or other carbonates are present in a groundwater system, they pre-empt the role of acid rain neutralization (Johnson 1984). The speed of the carbonate-acid reaction means that carbonates will control the acid neutralization chemistry of the system.

Although carbonate weathering reactions are relatively fast compared with the residence time of the groundwater in the TLW, certain aspects of the groundwater chemistry suggest, nevertheless, that they are not rapid enough to approach equilibrium under all the hydraulic and $H^+$ loadings experienced in the basin area. Berner (1978), and Plummer and Wigley (1976) concluded that for a pH between 4 and 6 in the natural environment, the weathering rate of calcite is primarily determined by the kinetics of surface reaction. That is, under most natural conditions the flushing rate and the degree of undersaturation have little effect on

the weathering rate. It follows that the kinetically determined carbonate weathering rate is the crucial factor determining the rate at which carbonate alkalinity is made available to neutralize acidic loadings in the groundwater.

This conclusion implies that the rate of carbonate weathering ought to be considered when estimating the ab'lity of groundwater to mitigate the effects of acid loading on an entire aquatic system. It is especially important to investigate and to consider this weathering rate or carbonate availibility because it seems not to increase in response to acid loading. The concentrations of $Ca^{2+}$ and $Mg^{2+}$ in the groundwater samples from well HU-0.67, for example, are approximately constant over time (Figure 5). Even during periods of rapid infiltration (rain or snowmelt) and rapid $H^{+}$ ion loading, the weathering rate of calcite appears not to change. Approximately the same amounts of $Ca^{2+}$ and $Mg^{2+}$, and thus of bicarbonate, are made available to the groundwater system at any given point in that system. As a result, sudden loadings of $H^{+}$ ions utilize all the available alkalinity, and the excess $H^{+}$ ion concentration is then expressed as a pH depression. As the pH drops below 5.0 the concentration of potassium ions in solution increases, possibly as a result of alumino-silicate alteration. The weathering of alumino-silicate minerals at pH's less than 5 will result in increased concentrations of Al in the groundwater. When the period of acid loading has passed, the carbonate weathering rate will once again be greater than the rate at which $H^{+}$ ions are being added to the system, and free bicarbonate ions will again become available. Thus even in groundwater

systems with measurable carbonate alkalinity, individual acid loading events may cause increased alumino-silicate alteration if the loading rate of $H^+$ exceeds the rate at which alkalinity is made available through carbonate weathering reactions.

In conclusion then, the acid neutralization capacity of the shallow surfical tills in the Turkey Lakes basin appears to be limited by the carbonate weathering rate. Groundwaters in these thin hillside tills show short term pH depressions due to rapid $H^+$ ion loadings, and during these periods they no longer provide a buffer retention system for the surface waters into which such groundwaters are discharged. This may represent the early stages of a development towards the levels of acidification observed in groundwaters in the Scandinavian Peninsula (Henriksen and Kirkhusmo 1982; Hultberg and Johansson 1981). If this is the case, and if acid loadings remain the same, over the long term we might expect increasing acidity in the surface waters of the Turkey Lakes basin and of similar watersheds in the Canadian Shield.

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## List of Figures

Figure 1: Turkey Lakes watershed showing location of groundwater instalations and sampling areas. HU area is at the east end of Lower Batchawana Lake (Headwater basin).

Figure 2: pH, alkalinity and groundwater level data from test well HU-0.67 for the period 24 March through early May. Note the pH and alkalinity depressions in conjunction with the rise in the watertable due to the March 27 rain and the main period of spring melt.

Figure 3: The concentration of $H^+$ and potassium ions over the time period of the pH depressions. Note the close relationship between the increase in $H^+$ concentration and the increase in potassium.

Figure 4: pH in the shallow groundwater vs the loading of $SO_4^{2-}$ and $NO_3^-$ from the bottom of the snow pack (loading data from Semkin and Jefferies, 1986).

Figure 5: Bar graph representing the concentration of $Ca^{2+}$, $Mg^{2+}$, and alkalinity over the time period of spring melt, 1985. Note that there is no marked increase in the concentration of $Ca^{2+}$ or $Mg^{2+}$ during those period when the bicarbonate drops to 0.

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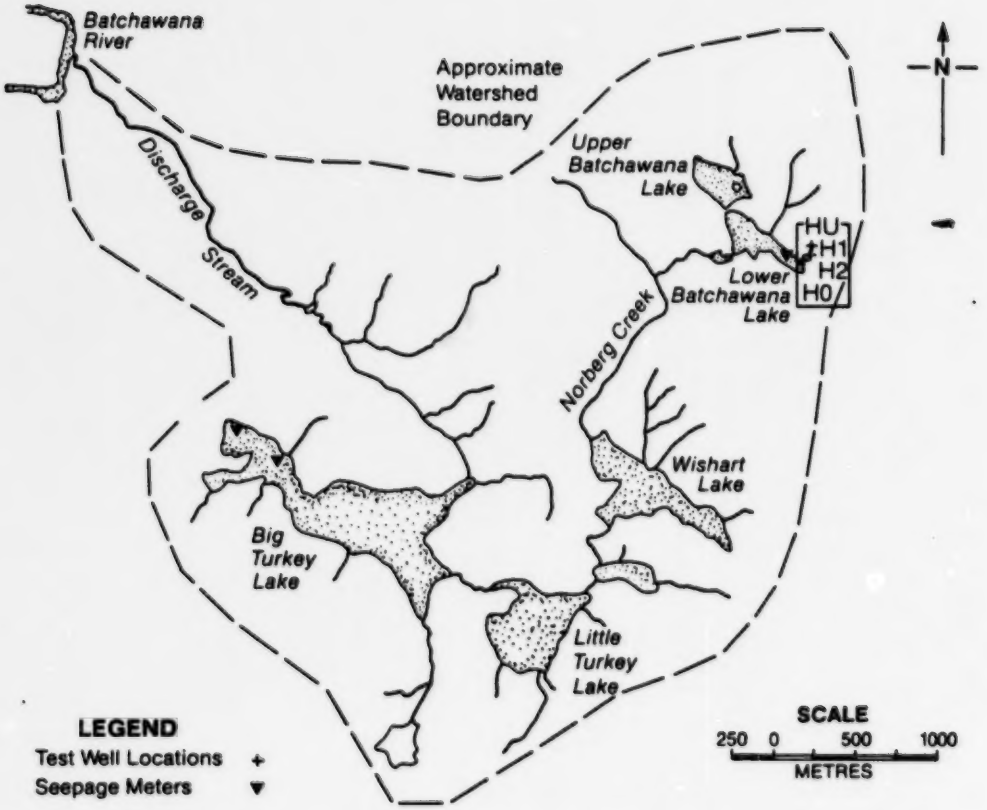
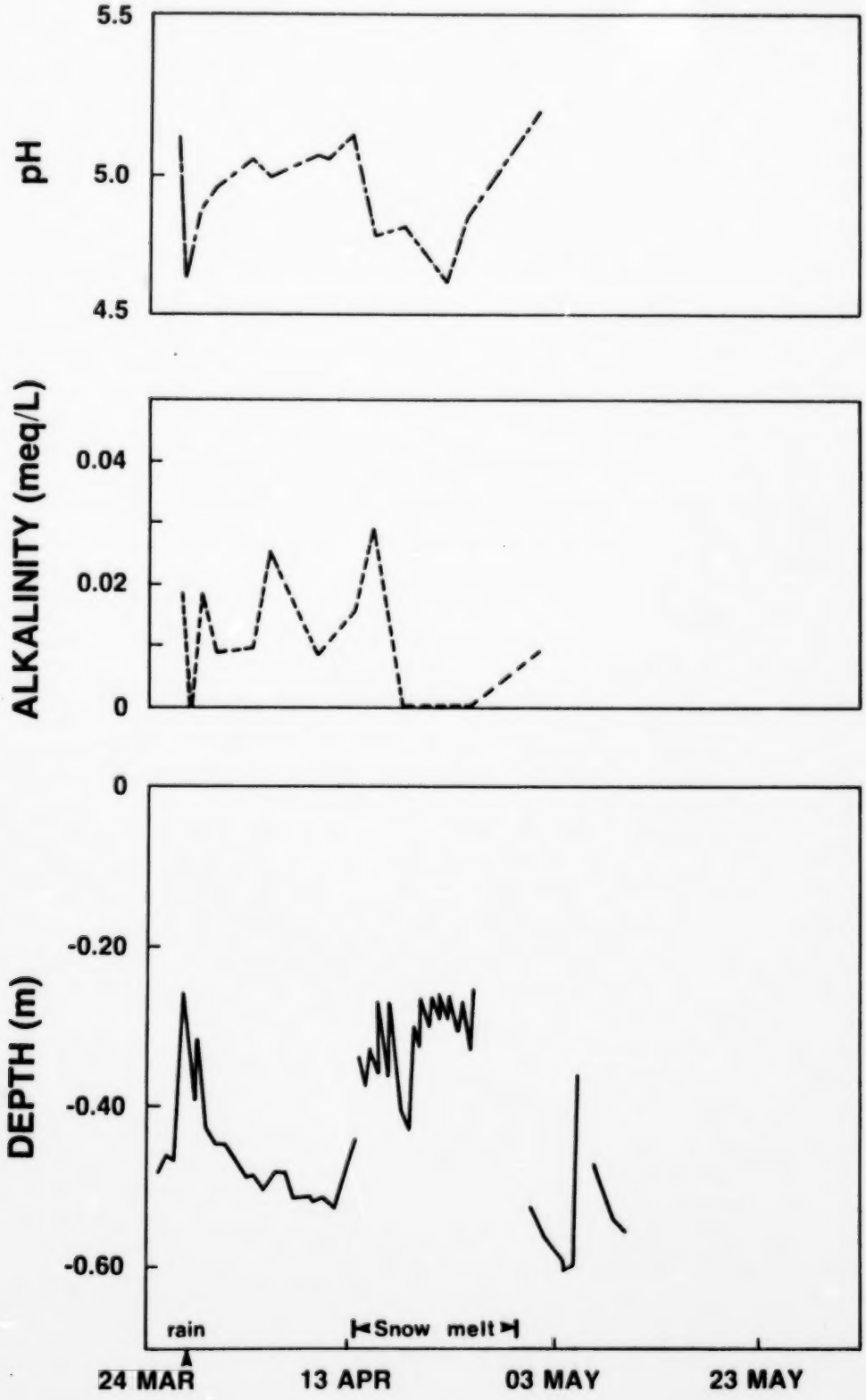
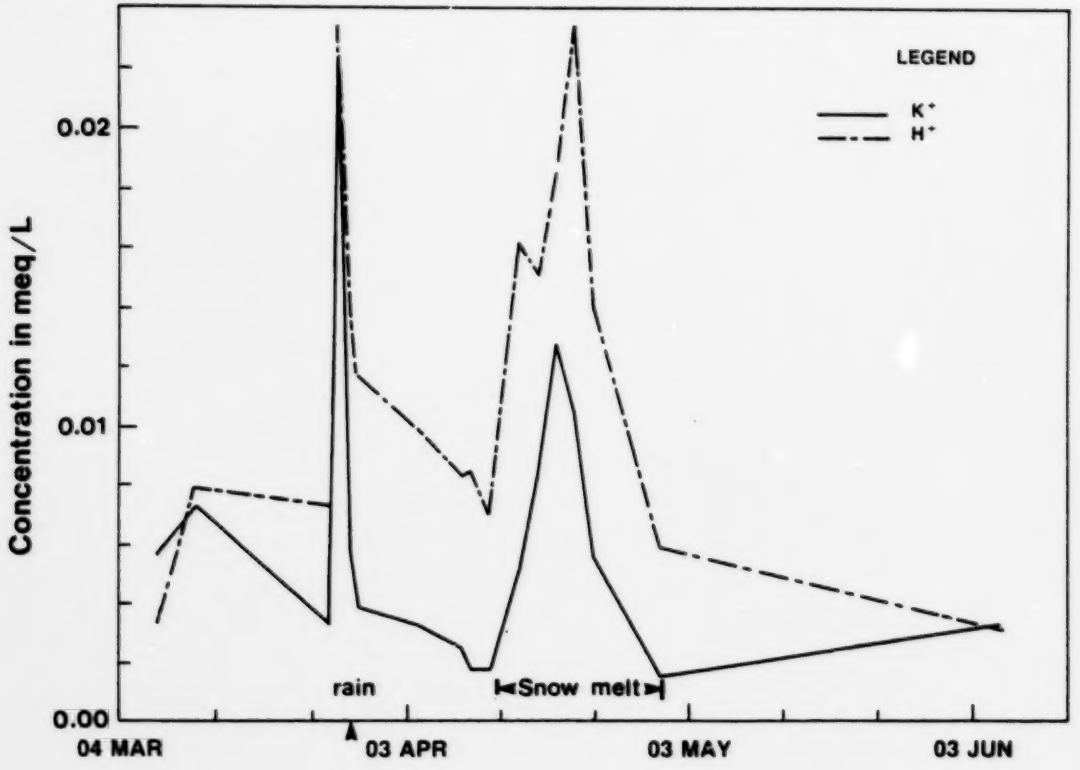
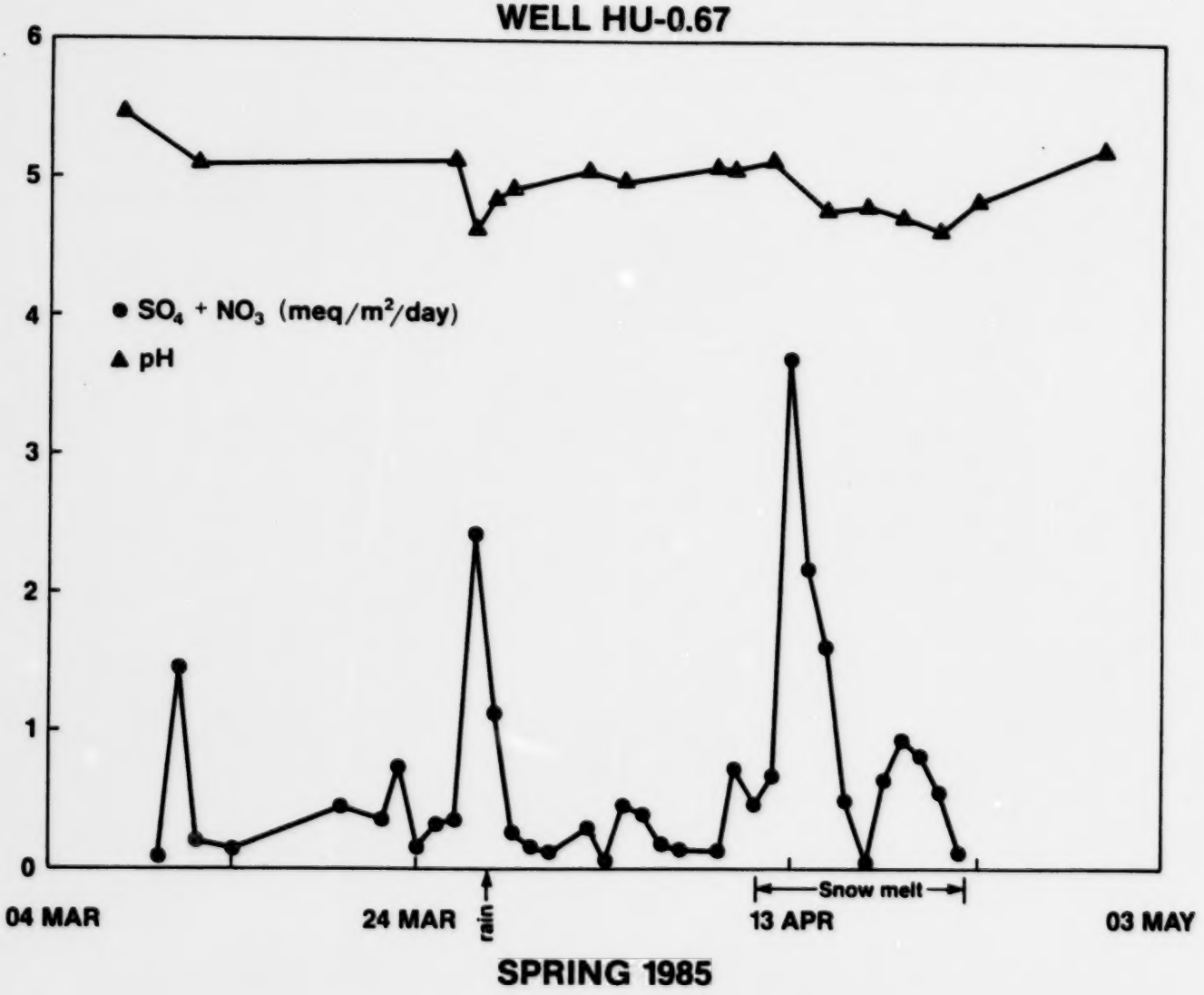
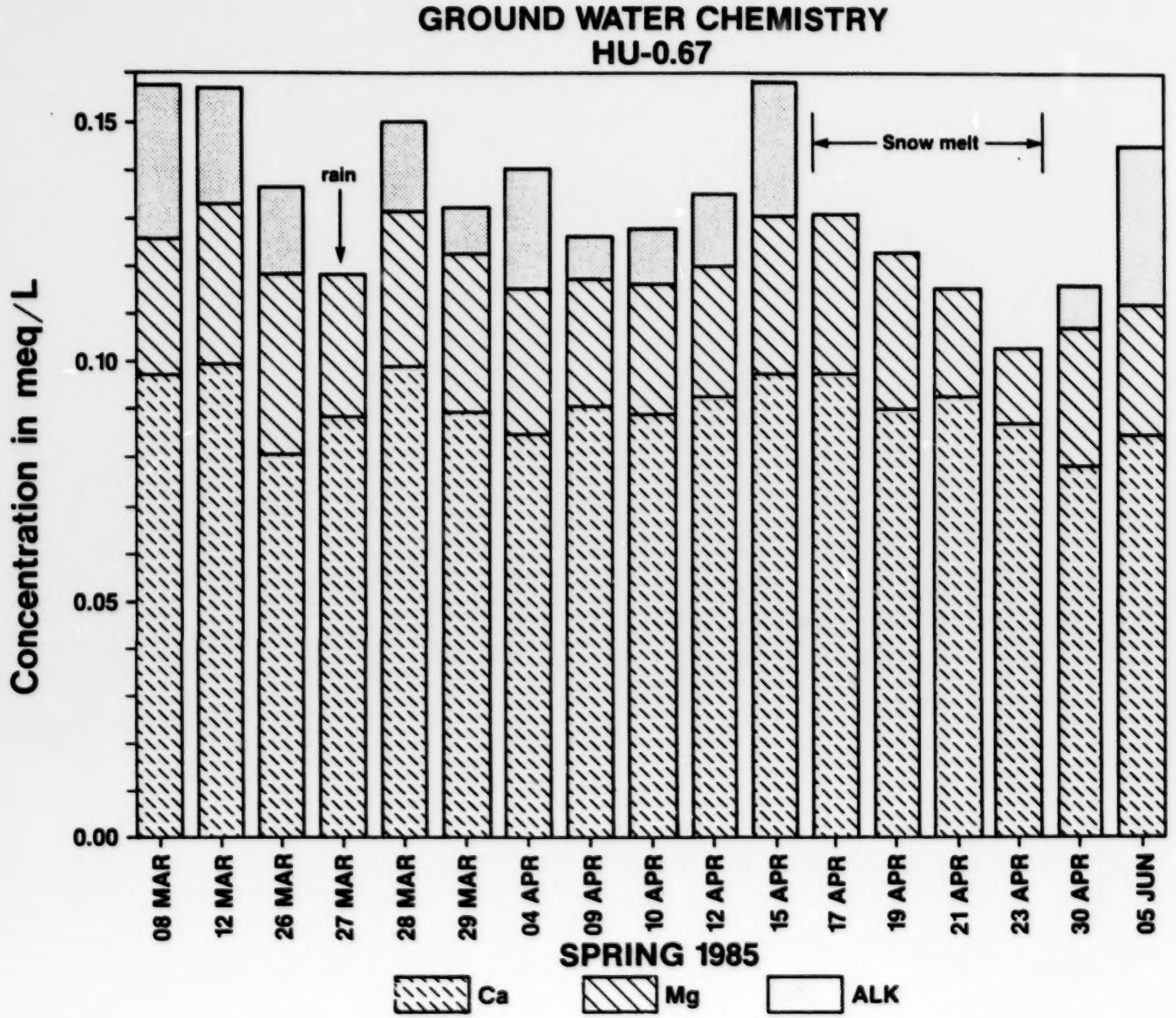

Batchawana River
Approximate Watershed Boundary
Upper Batchawana Lake
Discharge Stream
HU
H1
H2
H0
Lower Batchawana Lake
Norberg Creek
Wishart Lake
Big Turkey Lake
Little Turkey Lake
N
LEGEND
Test Well Locations
Seepage Meters
SCALE
250 0 500 1000
METRES


5.5
5.0
4.5
pH
0.04
0.02
0
ALKALINITY (meq/L)
0
-0.20
-0.40
-0.60
DEPTH (m)
rain
Snow melt
24 MAR
13 APR
03 MAY
23 MAY


LEGEND
K+
H+
Concentration in meq/L
0.02
0.01
0.00
rain
Snow melt
04 MAR
03 APR
03 MAY
03 JUN


WELL HU-0.67
6
5
4
3
2
1
0
● $SO_4$ + $NO_3$ (meq/$m^2$/day)
▲ pH
Snow melt
04 MAR
24 MAR
rain
13 APR
03 MAY

SPRING 1985


GROUND WATER CHEMISTRY
HU-0.67
Concentration in meq/L
0.15
0.10
0.05
0.00
rain
Snow melt
08 MAR
12 MAR
26 MAR
27 MAR
28 MAR
29 MAR
04 APR
09 APR
10 APR
12 APR
15 APR
17 APR
19 APR
21 APR
23 APR
30 APR
05 JUN
SPRING 1985
Ca
Mg
ALK